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TITLE: NEGATIVE ELECTRODE MATERIAL FOR NONAQUEOUS ELECTROLYTE
SECONDARY BATTERY

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide a negative electrode material for nonaqueous electrolyte second battery, capable of providing a nonaqueous electrolyte secondary battery having a high capacity and showing superior cycle properties.

SOLUTION: This negative electrode material for nonaqueous electrolyte secondary battery comprises a conductive SiOX powder, whose surface is covered with a conductive material having SiOX as a nucleus, by mechanically surface-fusing the conductive material of an average particle size d50(B) of 20 nm-30 μm to the SiOX powder of an average particle size d50(A) of 0.2-20 μm where the average particle size ratio d50(A)/d50(B) is 1.5 or larger.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the negative-electrode material for nonaqueous electrolyte rechargeable batteries which can attain improvement in the capacity of a nonaqueous electrolyte rechargeable battery, and improvement in cycle nature.

[0002]

[Description of the Prior Art] Although initial capacity improved sharply when SiOx powder was used as negative-electrode material for rechargeable lithium-ion batteries, there was a problem of cycle nature fall that the capacity falls by the charge and discharge of a repeat.

[0003] Although the report that cycle nature improves by carrying out after [mechanical alloying] carbonization processing of the SiO with a graphite is made by JP,2000-243396,A, this approach is unsuitable for production of a cost side to that a baking facility is the need or a industrial scale.

[0004] This invention aims at offering the negative-electrode material for nonaqueous electrolyte rechargeable batteries which could maintain high capacity, without falling cycle nature, and was suitable for industrial production, when it is made in view of the above-mentioned situation and uses for a nonaqueous electrolyte rechargeable battery.

[0005]

[The means for solving a technical problem and the gestalt of implementation of invention] The cause that cycle nature falls when SiOx powder is used as negative-electrode material as a result of repeating examination wholeheartedly, in order that this invention person may attain the above-mentioned purpose Since SiOx powder has low conductivity, Although conductivity is given by mixing a graphite and an amorphous carbon material as electric conduction material, and contacting a negative-electrode active material (SiOx) to electric conduction material in respect of a point While finding out that it is because the touch area of electric conduction material and a negative-electrode active material decreases and it becomes impossible to take a flow gradually by repeating expansion contraction of a negative-electrode active material in connection with charge and discharge By supporting or covering a conductive high ingredient with mechanical approaches, such as surface fusion equipment, on the front face of a negative-electrode active material, and uniting it with a negative-electrode active material by them, adhesion improved and collapse of the electrode by expansion contraction of a negative-electrode active material was controlled, and the knowledge of cycle nature improving is carried out, and it came to make this invention.

[0006] namely, electric conduction material matter [whose mean particle diameter d50 (B) is 20nm - 13 micrometers at the SiOx powder whose mean particle diameter d50 of this invention (A) is 0.2-20 micrometers -- however mean particle diameter -- a ratio -- d -- 50 -- (-- A --) -- /-- d -- 50 -- (-- B --) -- 1.5 -- more than -- it is --] -- mechanical -- a front face -- fusion -- processing -- carrying out -- things -- SiOx -- a nucleus -- ** -- carrying out -- a front face -- electric conduction -- material -- the matter -- having covered -- conductivity -- SiOx -- powder -- containing -- things - - the description -- ** -- carrying out -- nonaqueous electrolyte -- a rechargeable battery -- ** -- a negative electrode -- material -- providing .

[0007] Hereafter, lessons is taken from this invention and it explains in more detail. In this invention, the conductive SiOx powder which covered the front face by the electric conduction material matter by using SiOx as a nucleus by mechanical surface fusion processing is used for the negative-electrode material for nonaqueous electrolyte rechargeable batteries.

[0008] In this invention, usually obtain a silicon dioxide (SiO₂) and metal silicon (Si) as a raw material with SiOx. SiOx which is the generic name of the amorphous silicon oxide in which the value of x of SiOx is shown by 0 < x < 2, and is used by this invention The spectrum which the silicon oxide containing activity atom-like silicon has and by

which it is measured with the solid-state NMR of SiOx powder (29 SiDD/MAS) - The broadcloth peak centering on 70 ppm, especially the broadcloth peak in the range whose top-most vertices of a peak are -65--85ppm (A1), - It has separated into two peaks of the broadcloth peak (A2) in the range whose top-most vertices of the broadcloth peak centering on 110 ppm, especially a peak are -100--120ppm. And $0.1 \leq (A1)/(A2) \leq 1.0$ and that it is the range of $0.2 \leq (A1)/(A2) \leq 0.8$ have especially desirable surface ratio (A1)/(A2) of these peaks. if the value of surface ratio (A1)/(A2) becomes larger than 1.0 -- high -- although the rate of activity amorphous Si becomes large and the nonaqueous electrolyte rechargeable battery of high capacity is obtained, there is a possibility that cycle nature may fall.

[0009] On the other hand, as for the range of x of SiOx, it is desirable $x=0.6-1.5$ and that it is especially the positive number of 0.67-1.30. if the value of x is smaller than 0.6 -- high -- the rate of activity amorphous Si becomes large and the nonaqueous electrolyte rechargeable battery of high capacity has a possibility that the thing and cycle nature which are obtained may fall. Conversely, when the value of x is larger than 1.5, the rate of inactive SiO2 increases and there is a possibility that production of the nonaqueous electrolyte rechargeable battery of high capacity made into the purpose may become impossible.

[0010] In addition, for example, the oxygen analyzer in a ceramic (bottom scorification of an inactive air current) can analyze the amount of oxygen in SiOx. The above-mentioned range 0.6-1.5 of x is equivalent to about 25 - 46 % of the weight of abbreviation as an amount of oxygen.

[0011] 0.2-20 micrometers (A) of mean particle diameter d50 of the SiOx fine particles used for mechanical surface fusion processing are 0.5-10 micrometers preferably. In mean particle diameter smaller than 0.2 micrometers, the effect of scaling of a particle appears, the charge-and-discharge capacity of a negative-electrode active material decreases, and the spreading nature at the time of electrode production worsens in the mean particle diameter exceeding 20 micrometers. It can ask for this mean particle diameter d50 as a weighted mean value (or median size) in the particle-size-distribution measurement for example, by laser optical diffraction.

[0012] On the other hand in the constituted cell, that the electric conduction material matter should just be the ingredient of the electronic conduction nature which causes neither decomposition nor deterioration specifically Metal powder metallurgy group fiber, such as aluminum, Ti, Fe, nickel, Cu, Zn, Ag, Sn, and Si, Or even if graphites, such as mesophase carbon, a vapor growth carbon fiber, a pitch based carbon fiber, a PAN system carbon fiber, and various kinds of resin baking objects, etc. are used and it uses these independently in a natural graphite, an artificial graphite, and various kinds of end of a coke breeze Although you may use by two or more kinds, especially a graphite is suitably used for increase of the ease of carrying out of mechanical surface fusion, and the charge-and-discharge capacity per negative-electrode active material unit weight. Moreover, it is not limited especially about the configuration of the electric conduction material matter, either, but can use the shape of a globular shape, massive, and a scale, fibrous, etc.

[0013] 20nm - 13 micrometers (B) of mean particle diameter d50 of the powder of these electric conduction material matter are 35nm - 10 micrometers preferably. In mean particle diameter smaller than 20nm, the effect of scaling of a particle appears, conductivity falls, and the spreading nature at the time of electrode production worsens in the mean particle diameter exceeding 13 micrometers. In addition, although a usually available thing can be used for the powder of these electric conduction material matter, what ground suitably and was made into the above-mentioned mean-particle-diameter range may be used for it.

[0014] In this invention, the ratio $[d50 (A) / d50 (B)]$ of the mean particle diameter d50 of SiOx (A) to the mean particle diameter d50 of the electric conduction material matter (B) is preferably made or more into 2.0 1.5 or more. By making $d50 (A) / d50 (B)$ or more into 1.5, the surface area of the electric conduction material matter in contact with SiOx becomes large, consequently firm surface fusion is attained. Therefore, even if expansion contraction takes place at the time of charge and discharge, the exfoliation from the negative-electrode active material of the electric conduction material matter can be prevented, and cycle nature can improve by leaps and bounds by maintaining conductivity. If $d50 (A) / d50 (B)$ is smaller than 1.5 here, the surface area of the electric conduction material matter in contact with SiOx will be small, and the effectiveness of mechanical surface fusion will become small.

[0015] In addition, although the upper limit of the ratio $[d50 (A) / d50 (B)]$ of the mean particle diameter d50 of SiOx (A) to the mean particle diameter d50 of the electric conduction material matter (B) is selected suitably, it is desirable to make the value of $[d50 (A) / d50 (B)]$ especially or less into 20 500 or less. If the value of a mean-particle-diameter ratio exceeds 500, the particle diameter of the electric conduction material matter becomes fine too much, it becomes easy to disperse during mechanical surface fusion processing, and the effectiveness of mechanical surface fusion may become small.

[0016] The addition of the electric conduction material matter used for mechanical surface fusion processing is 5 - 40 % of the weight especially preferably one to 50% of the weight preferably. When the amount of the electric conduction material matter is made [more] than 50 % of the weight, there is a possibility that the conductivity of the electric

conduction material matter may fall with the advent of the field which detailed-ization of the particle by the collision of electric conduction material matter may take place, and does not participate in conductivity. When the addition of the electric conduction material matter is made into less than 1 % of the weight, there is a possibility that covering to a negative-electrode active material may become inadequate, and cycle nature may get worse from a conductive fall.

[0017] Here, there is an approach of putting raw material fine particles on the gas which exercises as the concrete approach of mechanical surface fusion processing, and throwing particles, or the approach of throwing fine particles at a firm wall, for example, a jet mill, hybridization, etc. are mentioned. Moreover, by letting narrow space pass by the big force etc., shearing force can be given to fine particles and the approach of using the energy in that case can also be taken. For example, the approach using mechano HYUJON [the Hosokawa Micron CORP. make] as this approach is mentioned. Furthermore, raw material fine particles and the movement object which is not related with a reaction can be put in into a pot, and the approach, for example, a ball mill, of giving the motion by which vibration, rotation, or these were combined with this, a vibration ball mill, a planet ball mill, a rolling ball mill, etc. can also be used.

[0018] In addition, to use these processings, a device is required for the order of materials charging and the mixed approach of raw material fine particles so that the electric conduction material matter may not be ground too much.

[0019] Although the thickness of the electric conduction material matter layer to cover changes with magnitude of the electric conduction material matter, 20nm - its 13 micrometers are desirable, and it is usually 35nm - 10 micrometers especially. If the thickness of the electric conduction material matter to cover is thinner than 20nm, electronic conduction nature may fall, and when thicker than 13 micrometers, there is a possibility that the diffusibility of electrolyte cations, such as a lithium ion to SiOx which is a negative-electrode active material, may fall.

[0020] As for the negative-electrode material of this invention, it is desirable that the carbon particle is included with above-mentioned conductive SiOx powder. In this case, although it is not limited and doping and undoping should be just possible in electrolyte cations, such as a lithium ion, especially as a carbon particle because of the improvement in charge-and-discharge capacity of the whole negative electrode, especially a graphite is desirable, and graphites, such as mesophase carbon, a vapor growth carbon fiber, a pitch based carbon fiber, a PAN system carbon fiber, and various kinds of resin baking objects, are usable, and, specifically, usable from a respectively amorphous thing to the thing of high crystallinity in a natural graphite, an artificial graphite, and various kinds of end of a coke breeze.

[0021] In this case, if many [if it is desirable that the carbon content in the mixture of conductive SiOx powder and a carbon particle is an amount used as 30 - 70 % of the weight 30 to 90% of the weight as for especially the mixed rate of the carbon particle to conductive SiOx powder and there are too few carbon contents in the above-mentioned mixture, cycle nature may get worse, and / too], charge-and-discharge capacity may decrease.

[0022] In this invention, the above-mentioned conductive SiOx powder and besides the mixture of this and a carbon particle being included preferably, binding material, such as polyvinylidene fluoride, and other well-known additives can be used for the negative electrode of a nonaqueous electrolyte rechargeable battery, and it can manufacture them with a conventional method.

[0023] Moreover, in the nonaqueous electrolyte rechargeable battery using the negative-electrode material of this invention, an ingredient, cell configurations, etc., such as a positive electrode, electrolytes (positive active material etc.), a non-aqueous solvent, and a separator, are not limited, for example, can use an oxide or a chalcogen compound of transition metals of LiCoO₂, LiNiO₂, LiMn₂O₄, V₂O₅, MnO₂ and TiS₂, and MoS₂ grade etc. as positive active material. As an electrolyte, the nonaqueous solution which contains lithium salt, such as lithium perchlorate, for example can be used, and solvents, such as propylene carbonate, ethylene carbonate, dimethoxyethane, gamma-butyl lactone, and 2-methyl tetrahydrofuran, can be used combining one sort or two sorts or more as a non-aqueous solvent. Moreover, the other various nonaqueous electrolyte and solid electrolytes can also be used.

[0024]

[Example] Although an example and the example of a comparison are given and this invention is explained concretely hereafter, this invention is not limited to the following example.

[0025] [example 1] silicon dioxide powder (BET specific surface area=200m²/g) and ceramic grade -- public funds -- equimolar came out of group silicon powder (BET specific surface area=4m²/g) comparatively, and it mixed. A reactor is filled up with this mixture and it decompresses to 0.1 or less Torrs, and SiOx gas was applied at the temperature up and the base made from SUS which holds, is made to generate SiOx gas and has carried out water cooling, and 1,350 degrees C was made to carry out a cooling deposit.

[0026] After collecting these sludges, the ball mill ground for 5 hours and SiOx powder was manufactured. The obtained SiOx powder was 8 micrometers in BET specific surface area 25m²/g and mean particle diameter, and was amorphous powder expressed with SiOx (x= 1.0).

[0027] It separated into two peaks, the broadcloth peak (A1) centering on -70 ppm, and the broadcloth peak (A2)

centering on -110 ppm, the spectrum measured with the solid-state NMR of the obtained SiOx powder (29 SiDD/MAS) was measured, and surface ratio (A1)/(A2) of these peaks was 0.65.

[0028] Mechanical surface fusion processing was performed for the above-mentioned SiOx powder [mean-particle-diameter d50(A)=8micrometer] for 30 minutes in nitrogen-gas-atmosphere mindg [20] [SiOx:C=8:2 (weight ratio)] Using 80g and an artificial graphite [mean-particle-diameter d50(B)=3micrometer]. Mechano HYUJON AM-15F by Hosokawa Micron CORP. were used for mechanical surface fusion processing. It became rotation casing which fixes fine particles to a wall with a centrifugal force from the inner piece which gives mechanical energy to the fine particles fixed to the casing inside, and the rotational frequency of casing set the gap of 2,500rpm, casing, and inner piece to 2mm. The oxygen density at the time of processing was 0.1% or less, and temperature was a maximum of 127 degrees C.

[0029] To the conductive SiOx powder obtained by carrying out mechanical surface fusion processing, in addition, the mixture of conductive SiOx powder and a graphite was obtained so that a carbonaceous rate might become 50% [SiOx:C=5:5 (weight ratio)] about an artificial graphite (mean particle diameter of 5 micrometers).

[0030] N-methyl pyrrolidone was added further and it considered as the slurry, in addition, this slurry was applied to copper foil with a thickness of 20 micrometers, and pressing of the electrode was carried out to the mixture of this conductive SiOx powder and graphite with the roller press after 1-hour desiccation at 120 degrees C so that it might become the rate of mixture:polyvinylidene fluoride =9:1 (weight ratio) of conductive SiOx powder and a graphite about polyvinylidene fluoride, and finally it pierced in diameter of 20mm, and considered as the negative electrode.

[0031] In order to evaluate the charge-and-discharge property of the negative electrode obtained here, the lithium foil was used for the counter electrode and the rechargeable lithium-ion battery for evaluation which used the fine porosity film with a thickness of 30 micrometers made from polyethylene for the separator was produced using the nonaqueous electrolyte solution which dissolved the 6 phosphorus-fluoride lithium in ethylene carbonate and 1, and 1/[of 2-dimethoxyethane] 1 (volume ratio) mixed liquor by the concentration of one mol / L as nonaqueous electrolyte.

[0032] After the produced rechargeable lithium-ion battery charged by 1mA constant current and amounted to 0V until the electrical potential difference of a test cell amounted to 0V using rechargeable battery charge and discharge test equipment [Made in Nagano], after leaving it at a room temperature overnight, it charged by decreasing a current so that a cel electrical potential difference might be kept at 0V. And when the current value was less than 20microA, charge was considered as termination. Discharge discharged by 1mA constant current, when the cel electrical potential difference exceeded 1.8V, it ended discharge, and it calculated discharge capacity. The above-mentioned actuation was repeated and the charge and discharge test of 10 cycles of the rechargeable lithium-ion battery for evaluation was performed. A result is shown in Table 1.

[0033] SiOx powder [mean-particle-diameter d50(A)=12micrometer] was obtained having used as 3 hours grinding time amount in the ball mill of the sludge obtained in the [example 2] example 1, and 20g of mechanical surface fusion processings was performed for this SiOx powder by the same approach as an example 1 using 80g and an artificial graphite [mean-particle-diameter d50(B)=3micrometer]. The oxygen density at the time of processing was 0.1% or less, and temperature was a maximum of 131 degrees C.

[0034] To the conductive SiOx powder obtained by carrying out mechanical surface fusion processing, in addition, the mixture of conductive SiOx powder and a graphite was obtained so that a carbonaceous rate might become 50% [SiOx:C=5:5 (weight ratio)] about a natural graphite (mean particle diameter of 5 micrometers). Using the mixture of this conductive SiOx powder and graphite, the negative electrode and the rechargeable lithium-ion battery for evaluation were produced by the same approach as an example 1, and the charge and discharge test was performed. A result is shown in Table 1.

[0035] [example 3] silicon dioxide powder (BET specific surface area=200m2/g) and ceramic grade -- public funds -- equimolar came out of group silicon powder (BET specific surface area=4m2/g) comparatively, and it mixed. A reactor is filled up with this mixture and it decompresses to 0.1 or less Torrs, and the temperature of a reactor was applied to the reactor, SiOx gas was applied to the temperature up and the base made from SUS which holds, is made to generate SiOx gas and has carried out water cooling with the sink at 1,350 degrees C, and the cooling deposit of the argon gas which mixed 20% of oxygen was carried out.

[0036] After collecting these sludges, the ball mill ground for 5 hours and SiOx powder was manufactured. The obtained SiOx powder was 8 micrometers in BET specific surface area210m2/g and mean particle diameter, and was amorphous powder expressed with SiOx (x= 1.22).

[0037] It separated into two peaks, the broadcloth peak (A1) centering on -70 ppm, and the broadcloth peak (A2) centering on -110 ppm, the spectrum measured with the solid-state NMR of the obtained SiOx powder (29 SiDD/MAS) was measured, and surface ratio (A1)/(A2) of these peaks was 0.27.

[0038] Mechanical surface fusion processing was performed for the above-mentioned SiOx powder [mean-particle-diameter $d_{50}(A)$ = 8micrometer] by the same approach as an example 1g [20] [SiOx:C=8:2 (weight ratio)] Using 80g and an artificial graphite [mean-particle-diameter $d_{50}(B)$ = 3micrometer]. The oxygen density at the time of processing was 0.1% or less, and temperature was a maximum of 121 degrees C.

[0039] To the conductive SiOx powder obtained by carrying out mechanical surface fusion processing, in addition, the mixture of conductive SiOx powder and a graphite was obtained so that a carbonaceous rate might become 50% [SiOx:C=5:5 (weight ratio)] about an artificial graphite (mean particle diameter of 5 micrometers). Using the mixture of this conductive SiOx powder and graphite, the negative electrode and the rechargeable lithium-ion battery for evaluation were produced by the same approach as an example 1, and the charge and discharge test was performed. A result is shown in Table 1.

[0040] Mechanical surface fusion processing was performed for the SiOx powder [mean-particle-diameter $d_{50}(A)$ = 8micrometer] of the [example 4] example 1 by the same approach as an example 1g [40] [SiOx:C=6:4 (weight ratio)] Using 60g and an artificial graphite [mean-particle-diameter $d_{50}(B)$ = 5micrometer]. The oxygen density at the time of processing was 0.1% or less, and temperature was a maximum of 78 degrees C.

[0041] To the conductive SiOx powder obtained by carrying out mechanical surface fusion processing, in addition, the mixture of conductive SiOx powder and a graphite was obtained so that a carbonaceous rate might become 50% [SiOx:C=5:5 (weight ratio)] about an artificial graphite (mean particle diameter of 5 micrometers). Using the mixture of this conductive SiOx powder and graphite, the negative electrode and the rechargeable lithium-ion battery for evaluation were produced by the same approach as an example 1, and the charge and discharge test was performed. A result is shown in Table 1.

[0042] The SiOx powder [mean-particle-diameter $d_{50}(A)$ = 8micrometer] of the [example 1 of comparison] example 1 was used without carrying out mechanical surface fusion processing, and to SiOx powder, in addition, the mixture of SiOx powder and a graphite was obtained so that a carbonaceous rate might become 50% [SiOx:C=5:5 (weight ratio)] about an artificial graphite (mean particle diameter of 3 micrometers). Using the mixture of this SiOx powder and graphite, the negative electrode and the rechargeable lithium-ion battery for evaluation were produced by the same approach as an example 1, and the charge and discharge test was performed. A result is shown in Table 1.

[0043] The SiOx powder [mean-particle-diameter $d_{50}(A)$ = 12micrometer] of the [example 2 of comparison] example 2 was used without carrying out mechanical surface fusion processing, and to SiOx powder, in addition, the mixture of SiOx powder and a graphite was obtained so that a carbonaceous rate might become 50% [SiOx:C=5:5 (weight ratio)] about an artificial graphite (mean particle diameter of 3 micrometers). Using the mixture of this SiOx powder and graphite, the negative electrode and the rechargeable lithium-ion battery for evaluation were produced by the same approach as an example 1, and the charge and discharge test was performed. A result is shown in Table 1.

[0044]

[Table 1]

	SiO _x /黒鉛の 平均粒子径比 $d_{50}(A)/d_{50}(B)$	最大放電容量 [mAh/g]	10サイクル目 [mAh/g]	サイクル保持率 [%]
実施例1	2.67	887	867	98
実施例2	4.00	893	857	96
実施例3	2.67	719	698	98
実施例4	1.60	863	723	84
比較例1	2.67	763	511	67
比較例2	4.00	783	556	71

[0045]

[Effect of the Invention] According to this invention, the negative-electrode material for nonaqueous electrolyte rechargeable batteries which gives the nonaqueous electrolyte rechargeable battery in which high capacity and the outstanding cycle nature are shown is obtained.

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CLAIMS

[Claim(s)]

[Claim 1] mean particle diameter -- d -- 50 -- (-- A --) -- 0.2 - 20 -- micrometer -- it is -- SiOx -- powder -- mean particle diameter -- d -- 50 -- (-- B --) -- 20 -- nm - 13 -- micrometer -- it is -- electric conduction -- material -- the matter -- [-- however -- mean particle diameter -- a ratio -- d -- 50 -- (-- A --) -- /-- d -- 50 -- (-- B --) -- 1.5 -- more than -- it is --] -- mechanical -- a front face -- fusion -- processing -- carrying out -- things -- SiOx -- a nucleus -- ** -- carrying out -- a front face -- electric conduction -- material -- the matter -- having covered -- conductivity -- SiOx -- powder -- containing -- things -- the description -- ** -- carrying out -- nonaqueous electrolyte -- a rechargeable battery -- ** -- a negative electrode -- material .

[Claim 2] Negative-electrode material for nonaqueous electrolyte rechargeable batteries characterized by for the amount of the electric conduction material matter in conductive SiOx powder being 1 - 50 % of the weight to the sum total of SiOx powder and the electric conduction material matter, and the carbon content in the mixture of conductive SiOx powder and a carbon particle being 30 - 90 % of the weight including the mixture of a conductive SiOx powder and a carbon particle according to claim 1.

[Claim 3] Negative-electrode material for nonaqueous electrolyte rechargeable batteries according to claim 1 characterized by the thickness of a wrap electric conduction material matter layer being 20nm - 13 micrometers about a SiOx powder front face.

[Claim 4] The broadcloth peak [spectrum / by which SiOx powder is measured with the solid-state NMR (29 SiDD/MAS)] centering on -70 ppm (A1), - Negative-electrode material for nonaqueous electrolyte rechargeable batteries according to claim 1 which has separated into two peaks of the broadcloth peak (A2) centering on 110 ppm, and is characterized by the range of surface ratio (A1)/(A2) of these peaks being $0.1 \leq (A1)/(A2) \leq 1.0$.

[Claim 5] Negative-electrode material for nonaqueous electrolyte rechargeable batteries according to claim 1 characterized by the value of x of SiOx being the positive number of the range of $0.6 \leq x \leq 1.5$.

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(54) 【発明の名称】 非水電解質二次電池用負極材

(57) 【要約】

【解決手段】 平均粒子径 d_{50} (A) が $0.2 \sim 20 \mu\text{m}$ の SiO_x 粉末に平均粒子径 d_{50} (B) が $20 \text{nm} \sim 13 \mu\text{m}$ の導電材物質〔但し、平均粒子径比 d_{50} (A) / d_{50} (B) は 1.5 以上である〕を機械的 surface 融合処理することにより SiO_x を核として表面を導電材物質で覆った導電性 SiO_x 粉末を含むことを特徴とする非水電解質二次電池用負極材。

【効果】 本発明によれば、高容量かつ優れたサイクル性を示す非水電解質二次電池を与える非水電解質二次電池用負極材が得られる。

【特許請求の範囲】

【請求項1】 平均粒子径 d_{50} (A) が $0.2 \sim 20 \mu\text{m}$ の SiO_x 粉末に平均粒子径 d_{50} (B) が $20 \text{nm} \sim 13 \mu\text{m}$ の導電材物質〔但し、平均粒子径比 d_{50} (A) / d_{50} (B) は 1.5 以上である〕を機械的表面融合処理することにより SiO_x を核として表面を導電材物質で覆った導電性 SiO_x 粉末を含むことを特徴とする非水電解質二次電池用負極材。

【請求項2】 請求項1記載の導電性 SiO_x 粉末と炭素粒子との混合物を含み、導電性 SiO_x 粉末中の導電材物質の量が、 SiO_x 粉末と導電材物質の合計に対し $1 \sim 50$ 重量%であり、導電性 SiO_x 粉末と炭素粒子との混合物中の炭素量が $30 \sim 90$ 重量%であることを特徴とする非水電解質二次電池用負極材。

【請求項3】 SiO_x 粉末表面を覆う導電材物質層の厚さが $20 \text{nm} \sim 13 \mu\text{m}$ であることを特徴とする請求項1記載の非水電解質二次電池用負極材。

【請求項4】 SiO_x 粉末が、その固体NMR ($^{29}\text{Si DD/MAS}$) により測定されるスペクトルが、 -70ppm を中心としたブロードなピーク (A1) と、 -110ppm を中心としたブロードなピーク (A2) の2つのピークとに分離しており、かつこれらのピークの面積比 (A1) / (A2) が $0.1 \leq (A1) / (A2) \leq 1.0$ の範囲であることを特徴とする請求項1記載の非水電解質二次電池用負極材。

【請求項5】 SiO_x の x の値が $0.6 \leq x \leq 1.5$ の範囲の正数であることを特徴とする請求項1記載の非水電解質二次電池用負極材。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水電解質二次電池の容量の向上と、サイクル性の向上を達成できる非水電解質二次電池用負極材に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】リチウムイオン二次電池用負極材として SiO_x 粉末を用いた場合には、初期容量は大幅に向上するものの、繰り返しの充放電によりその容量が低下するというサイクル性低下の問題があった。

【0003】特開2000-243396号公報には、 SiO を黒鉛とメカニカルアロイング後炭化処理することにより、サイクル性が向上するという報告がなされているが、この方法は、焼成設備が必要なことやコスト面から工業的規模の生産には不向きである。

【0004】本発明は、上記事情に鑑みなされたものであり、非水電解質二次電池に用いた場合、サイクル性を低下することなく高容量を維持でき、かつ工業的生産に適した非水電解質二次電池用負極材を提供することを目的とする。

【0005】

【課題を解決するための手段及び発明の実施の形態】本発明者は、上記目的を達成するため鋭意検討を重ねた結果、負極材として SiO_x 粉末を用いた場合にサイクル性が低下する原因が、 SiO_x 粉末は導電性が低いため、導電材として黒鉛や非晶質の炭素材料を混合し、導電材と負極活物質 (SiO_x) を点又は面で接触させることにより導電性を持たせているが、充放電に伴い負極活物質の膨張収縮が繰り返されることにより、導電材と負極活物質との接触面積が減少し、導通が次第にとれなくなるためであることを見出すと共に、導電性の高い材料を表面融合装置等の機械的な方法で、負極活物質の表面に担持又は被覆し、負極活物質と融合させることで、密着性が向上し、負極活物質の膨張収縮による電極の崩壊が抑制され、サイクル性が向上することを見出し本発明をなすに至った。

【0006】即ち、本発明は、平均粒子径 d_{50} (A) が $0.2 \sim 20 \mu\text{m}$ の SiO_x 粉末に平均粒子径 d_{50} (B) が $20 \text{nm} \sim 13 \mu\text{m}$ の導電材物質〔但し、平均粒子径比 d_{50} (A) / d_{50} (B) は 1.5 以上である〕を機械的表面融合処理することにより SiO_x を核として表面を導電材物質で覆った導電性 SiO_x 粉末を含むことを特徴とする非水電解質二次電池用負極材を提供する。

【0007】以下、本発明につき更に詳しく説明する。本発明では、機械的表面融合処理により SiO_x を核として表面を導電材物質で覆った導電性 SiO_x 粉末を非水電解質二次電池用負極材に使用する。

【0008】本発明において SiO_x とは通常、二酸化ケイ素 (SiO_2) と金属ケイ素 (Si) とを原料として得られる、 SiO_x の x の値が $0 < x < 2$ で示される非晶質のケイ素酸化物の総称であり、本発明で用いられる SiO_x は、活性な原子状ケイ素を含むケイ素酸化物が好ましく、 SiO_x 粉末の固体NMR ($^{29}\text{Si DD/MAS}$) により測定されるスペクトルが、 -70ppm を中心としたブロードなピーク、特にピークの頂点が $-65 \sim -85 \text{ppm}$ の範囲にあるブロードなピーク (A1) と、 -110ppm を中心としたブロードなピーク、特にピークの頂点が $-100 \sim -120 \text{ppm}$ の範囲にあるブロードなピーク (A2) の2つのピークに分離しており、かつこれらのピークの面積比 (A1) / (A2) が $0.1 \leq (A1) / (A2) \leq 1.0$ 、特に $0.2 \leq (A1) / (A2) \leq 0.8$ の範囲であることが好ましい。面積比 (A1) / (A2) の値が 1.0 より大きくなると、高活性な非晶質 Si の割合が大きくなり、高容量の非水電解質二次電池は得られるものの、サイクル性が低下してしまう恐れがある。

【0009】一方、 SiO_x の x の範囲は $x = 0.6 \sim 1.5$ 、特に $0.67 \sim 1.30$ の正数であることが好ましい。 x の値が 0.6 より小さいと高活性な非晶質 Si の割合が大きくなり、高容量の非水電解質二次電池は

得られるもの、サイクル性が低下してしまう恐れがある。逆にxの値が1.5より大きいと、不活性な SiO_2 の割合が増加し、目的とする高容量の非水電解質二次電池の作製ができなくなる恐れがある。

【0010】なお、 SiO_x 中の酸素量は、例えば、セラミック中酸素分析装置（不活性気流下溶融法）により分析することができる。上記のxの範囲0.6～1.5は、酸素量として約25～約46重量％に相当する。

【0011】機械的表面融合処理に用いる SiO_x 粉体の平均粒子径 d_{50} (A)は0.2～20 μm 、好ましくは0.5～10 μm である。0.2 μm より小さい平均粒子径では、粒子の表面酸化の影響が表れ、負極活物質の充放電容量が減少し、20 μm を超える平均粒子径では電極作製時の塗布性が悪くなる。この平均粒子径 d_{50} は、例えばレーザー光回折法による粒度分布測定における重量平均値（或いはメジアン径）として求めることができる。

【0012】一方、導電材物質は、構成された電池において、分解や変質を起こさない電子伝導性の材料であればよく、具体的には、Al、Ti、Fe、Ni、Cu、Zn、Ag、Sn、Si等の金属粉末や金属繊維、又は天然黒鉛、人造黒鉛、各種のコークス粉末、メソフェーズ炭素、気相成長炭素繊維、ピッチ系炭素繊維、PAN系炭素繊維、各種の樹脂焼成体等の黒鉛等が用いられ、これらは単独で用いても、2種類以上で用いてもよいが、機械的表面融合のしやすさ及び負極活物質単位重量当たりの充放電容量の増大のため、特に黒鉛が好適に用いられる。また、導電材物質の形状についても特に限定されず、球状、塊状、鱗片状、繊維状等が使用できる。

【0013】これら導電材物質の粉末は、平均粒子径 d_{50} (B)が20nm～13 μm 、好ましくは35nm～10 μm である。20nmより小さい平均粒子径では、粒子の表面酸化の影響が表れ、導電性が低下し、13 μm を超える平均粒子径では電極作製時の塗布性が悪くなる。なお、これらの導電材物質の粉末は、通常入手可能なものが使用できるが、適宜粉砕して上記平均粒子径範囲としたものを用いてもよい。

【0014】本発明においては、導電材物質の平均粒子径 d_{50} (B)に対する、 SiO_x の平均粒子径 d_{50} (A)の比 $[d_{50} \text{ (A)} / d_{50} \text{ (B)}]$ を1.5以上、好ましくは2.0以上とする。 $d_{50} \text{ (A)} / d_{50} \text{ (B)}$ を1.5以上とすることで、 SiO_x と接触する導電材物質の表面積が大きくなり、その結果、強固な表面融合化が可能となる。従って、充放電時に膨張収縮が起こっても、導電材物質の負極活物質からの剥離が防止でき、導電性を維持することでサイクル性が飛躍的に向上することができる。ここで $d_{50} \text{ (A)} / d_{50} \text{ (B)}$ が1.5より小さいと SiO_x に接触する導電材物質の表面積が小さく、機械的表面融合の効果が小さくなってしまふ。

【0015】なお、導電材物質の平均粒子径 d_{50} (B)に対する、 SiO_x の平均粒子径 d_{50} (A)の比 $[d_{50} \text{ (A)} / d_{50} \text{ (B)}]$ の上限は適宜選定されるが、 $[d_{50} \text{ (A)} / d_{50} \text{ (B)}]$ の値を500以下、特に20以下にすることが好ましい。平均粒子径比の値が500を超えると導電材物質の粒子径が細くなりすぎ、機械的表面融合処理中に飛散しやすくなり、機械的表面融合化の効果が小さくなってしまふ場合がある。

【0016】機械的表面融合処理に用いる導電材物質の添加量は、好ましくは1～50重量％、特に好ましくは5～40重量％である。導電材物質の量を50重量％より多くした場合、導電材物質同士の衝突による粒子の微細化が起こる場合があり、導電性に関与しない面の出現により導電材物質の導電性が低下する恐れがある。導電材物質の添加量を1重量％未満とした場合、負極活物質への被覆が不十分となる場合があり、導電性の低下からサイクル性が悪化する恐れがある。

【0017】ここで、機械的表面融合処理の具体的な方法としては、原料粉体を運動する気体にのせて粒子同士をぶつける方法、又は粉体を強固な壁にぶつける方法があり、例えばジェットミル、ハイブリダイゼーション等が挙げられる。また、狭い空間を大きな力で通す等の方法により、粉体にせん断力を与えて、その際のエネルギーを利用する方法を採ることもできる。この方法としては、例えばメカノヒュージョン〔ホソカワミクロン（株）製〕を用いる方法が挙げられる。更に、ボット中に原料粉体と反応に関与しない運動体を入れて、これに振動、回転又はこれらが組み合わされた動きを与える方法、例えばボールミル、振動ボールミル、遊星ボールミル、転動ボールミル等を用いることもできる。

【0018】なお、これらの処理を用いる場合には、導電材物質を過度に粉砕してしまわないように、原料粉体の投入順序や混合方法に工夫が必要である。

【0019】被覆する導電材物質層の厚さは、導電材物質の大きさによって異なるが、通常20nm～13 μm が好ましく、特に35nm～10 μm である。被覆する導電材物質の厚さが20nmより薄いと、電子伝導性が低下する場合があり、13 μm より厚いと、負極活物質である SiO_x へのリチウムイオン等の電解質カチオンの拡散性が低下する恐れがある。

【0020】本発明の負極材は、上述の導電性 SiO_x 粉末と共に、炭素粒子を含んでいることが好ましい。この場合炭素粒子としては、特に限定されるものではなく、負極全体の充放電容量向上のため、リチウムイオン等の電解質カチオンをドーピング、脱ドーピング可能なものであればよいが、特に黒鉛が好ましく、具体的には、天然黒鉛、人造黒鉛、各種のコークス粉末、メソフェーズ炭素、気相成長炭素繊維、ピッチ系炭素繊維、PAN系炭素繊維、各種の樹脂焼成体等の黒鉛が使用可能であり、それぞれ非晶質のものから高結晶性のものまで

使用可能である。

【0021】この場合、導電性 SiO_x 粉末に対する炭素粒子の混合割合は、導電性 SiO_x 粉末と炭素粒子との混合物中の炭素量が30～90重量%、特に30～70重量%となる量であることが好ましく、上記混合物中の炭素量が少なすぎると、サイクル性が悪化する場合があり、多すぎると、充放電容量が減少する場合がある。

【0022】本発明において、非水電解質二次電池の負極は、上記導電性 SiO_x 粉末、好ましくはこれと炭素粒子との混合物を含む以外に、ポリフッ化ビニリデン等の結着材、その他公知の添加剤を用いて常法により製造することができる。

【0023】また、本発明の負極材を用いた非水電解質二次電池においては、正極（正極活物質等）、電解質、非水溶媒、セパレータ等の材料及び電池形状等は限定されず、例えば、正極活物質としては、 LiCoO_2 、 LiNiO_2 、 LiMn_2O_4 、 V_2O_5 、 MnO_2 、 TiS_2 、 MoS_2 等の遷移金属の酸化物又はカルコゲン化合物等を用いることができる。電解質としては、例えば過塩素酸リチウム等のリチウム塩を含む非水溶液を用いることができ、非水溶媒としてはプロピレンカーボネート、エチレンカーボネート、ジメトキシエタン、 γ -ブチラクトン、2-メチルテトラヒドロフラン等の溶媒を1種又は2種以上を組み合わせ用いることができる。また、それ以外の種々の非水電解質や固体電解質も使用できる。

【0024】

【実施例】以下、実施例及び比較例を挙げて本発明を具体的に説明するが、本発明は下記実施例に限定されるものではない。

【0025】[実施例1] 二酸化珪素粉末（BET比表面積＝ $200\text{m}^2/\text{g}$ ）とセラミックグレード用金属ケイ素粉末（BET比表面積＝ $4\text{m}^2/\text{g}$ ）を等モルの割合で混合した。この混合物を反応器に充填し、0.1 Torr以下に減圧し、1,350℃に昇温、保持して SiO_x ガスを発生させ、水冷してあるSUS製の基体に SiO_x ガスを当てて冷却析出させた。

【0026】この析出物を回収した後、ボールミルで5時間粉碎し、 SiO_x 粉末を製造した。得られた SiO_x 粉末は、BET比表面積 $25\text{m}^2/\text{g}$ 、平均粒子径 $8\mu\text{m}$ であり、 SiO_x （ $x=1.0$ ）で表される非晶質粉末であった。

【0027】得られた SiO_x 粉末の固体NMR（ ^{29}Si DD/MAS）により測定されたスペクトルは、 -70ppm を中心としたブロードなピーク（A1）と、 -110ppm を中心としたブロードなピーク（A2）の2つのピークに分離して測定され、これらのピークの面積比（A1）／（A2）は0.65であった。

【0028】上記 SiO_x 粉末[平均粒子径 d_{50} （A）＝ $8\mu\text{m}$]を80g、人造黒鉛[平均粒子径 d_{50} （B）

＝ $3\mu\text{m}$]を20g [SiO_x ：C＝8：2（重量比）]用い、窒素雰囲気中で30分間、機械的表面融合処理を行った。機械的表面融合処理には、ホソカワミクロン（株）製のメカノヒュージョンAM-15Fを用いた。遠心力で内壁に粉体を固定する回転ケーシングと、ケーシング内面に固定された粉体に、機械的エネルギーを付与するインナーピースからなり、ケーシングの回転数は2,500rpm、ケーシングとインナーピースとの間隙は2mmとした。処理時の酸素濃度は0.1%以下であり、温度は最高127℃であった。

【0029】機械的表面融合処理して得られた導電性 SiO_x 粉末に、人造黒鉛（平均粒子径 $5\mu\text{m}$ ）を炭素の割合が50% [SiO_x ：C＝5：5（重量比）]となるように加え導電性 SiO_x 粉末と黒鉛との混合物を得た。

【0030】この導電性 SiO_x 粉末と黒鉛との混合物に、ポリフッ化ビニリデンを、導電性 SiO_x 粉末と黒鉛との混合物：ポリフッ化ビニリデン＝9：1（重量比）の割合になるように加え、更にN-メチルピロリドンを加えスラリーとし、このスラリーを厚さ $20\mu\text{m}$ の銅箔に塗布し、120℃で1時間乾燥後、ローラープレスにより電極を加圧成形し、最終的には直径20mmに打ち抜き負極とした。

【0031】ここで得られた負極の充放電特性を評価するために、対極にリチウム箔を使用し、非水電解質として六フッ化リンリチウムをエチレンカーボネートと1，2-ジメトキシエタンの1／1（体積比）混合液に1モル／Lの濃度で溶解した非水電解質溶液を用い、セパレータに厚さ $30\mu\text{m}$ のポリエチレン製微多孔質フィルムを用いた評価用リチウムイオン二次電池を作製した。

【0032】作製したリチウムイオン二次電池は、一晩室温で放置した後、二次電池充放電試験装置〔（株）ナガノ製〕を用い、テストセルの電圧が0Vに達するまで1mAの定電流で充電を行い、0Vに達した後は、セル電圧を0Vに保つように電流を減少させて充電を行った。そして、電流値が $20\mu\text{A}$ を下回った時点で充電を終了とした。放電は1mAの定電流で放電を行い、セル電圧が1.8Vを上回った時点で放電を終了し、放電容量を求めた。上記の操作を繰り返し、評価用リチウムイオン二次電池の10サイクルの充放電試験を行った。結果を表1に示す。

【0033】[実施例2] 実施例1で得られた析出物のボールミルでの粉碎時間を3時間として、 SiO_x 粉末[平均粒子径 d_{50} （A）＝ $12\mu\text{m}$]を得、この SiO_x 粉末を80g、人造黒鉛[平均粒子径 d_{50} （B）＝ $3\mu\text{m}$]を20g用い、実施例1と同様の方法で機械的表面融合処理を行った。処理時の酸素濃度は0.1%以下であり、温度は最高131℃であった。

【0034】機械的表面融合処理して得られた導電性 SiO_x 粉末に、天然黒鉛（平均粒子径 $5\mu\text{m}$ ）を炭素の

割合が50% [$\text{SiO}_x : \text{C} = 5 : 5$ (重量比)] となるように加え導電性 SiO_x 粉末と黒鉛との混合物を得た。この導電性 SiO_x 粉末と黒鉛との混合物を用いて、実施例1と同様の方法にて負極及び評価用リチウムイオン二次電池を作製し、充放電試験を行った。結果を表1に示す。

【0035】[実施例3] 二酸化珪素粉末 (BET比表面積 $=200\text{m}^2/\text{g}$) とセラミックグレード用金属ケイ素粉末 (BET比表面積 $=4\text{m}^2/\text{g}$) を等モルの割合で混合した。この混合物を反応器に充填し、0.1 Torr以下に減圧し、20%の酸素を混合したアルゴンガスを反応器に流しながら反応器の温度を1,350℃に昇温、保持して SiO_x ガスを発生させ、水冷してあるSUS製の基体に SiO_x ガスを当てて冷却析出させた。

【0036】この析出物を回収した後、ボールミルで5時間粉碎し、 SiO_x 粉末を製造した。得られた SiO_x 粉末は、BET比表面積 $210\text{m}^2/\text{g}$ 、平均粒子径 $8\mu\text{m}$ であり、 SiO_x ($x=1.22$) で表される非晶質粉末であった。

【0037】得られた SiO_x 粉末の固体NMR (^{29}Si IDDMAS) により測定されたスペクトルは、 -70ppm を中心としたブロードなピーク (A1) と、 -110ppm を中心としたブロードなピーク (A2) の2つのピークに分離して測定され、これらのピークの面積比 (A1)/(A2) は0.27であった。

【0038】上記 SiO_x 粉末 [平均粒子径 d_{50} (A) $=8\mu\text{m}$] を80g、人造黒鉛 [平均粒子径 d_{50} (B) $=3\mu\text{m}$] を20g [$\text{SiO}_x : \text{C} = 8 : 2$ (重量比)] 用い、実施例1と同様の方法で機械的表面融合処理を行った。処理時の酸素濃度は0.1%以下であり、温度は最高121℃であった。

【0039】機械的表面融合処理して得られた導電性 SiO_x 粉末に、人造黒鉛 (平均粒子径 $5\mu\text{m}$) を炭素の割合が50% [$\text{SiO}_x : \text{C} = 5 : 5$ (重量比)] となるように加え導電性 SiO_x 粉末と黒鉛との混合物を得た。この導電性 SiO_x 粉末と黒鉛との混合物を用い

*て、実施例1と同様の方法にて負極及び評価用リチウムイオン二次電池を作製し、充放電試験を行った。結果を表1に示す。

【0040】[実施例4] 実施例1の SiO_x 粉末 [平均粒子径 d_{50} (A) $=8\mu\text{m}$] を60g、人造黒鉛 [平均粒子径 d_{50} (B) $=5\mu\text{m}$] を40g [$\text{SiO}_x : \text{C} = 6 : 4$ (重量比)] 用い、実施例1と同様の方法で機械的表面融合処理を行った。処理時の酸素濃度は0.1%以下であり、温度は最高78℃であった。

10 【0041】機械的表面融合処理して得られた導電性 SiO_x 粉末に、人造黒鉛 (平均粒子径 $5\mu\text{m}$) を炭素の割合が50% [$\text{SiO}_x : \text{C} = 5 : 5$ (重量比)] となるように加え導電性 SiO_x 粉末と黒鉛との混合物を得た。この導電性 SiO_x 粉末と黒鉛との混合物を用いて、実施例1と同様の方法にて負極及び評価用リチウムイオン二次電池を作製し、充放電試験を行った。結果を表1に示す。

20 【0042】[比較例1] 実施例1の SiO_x 粉末 [平均粒子径 d_{50} (A) $=8\mu\text{m}$] を機械的表面融合処理せずに用い、 SiO_x 粉末に、人造黒鉛 (平均粒子径 $3\mu\text{m}$) を炭素の割合が50% [$\text{SiO}_x : \text{C} = 5 : 5$ (重量比)] となるように加え SiO_x 粉末と黒鉛との混合物を得た。この SiO_x 粉末と黒鉛との混合物を用いて、実施例1と同様の方法にて負極及び評価用リチウムイオン二次電池を作製し、充放電試験を行った。結果を表1に示す。

30 【0043】[比較例2] 実施例2の SiO_x 粉末 [平均粒子径 d_{50} (A) $=12\mu\text{m}$] を機械的表面融合処理せずに用い、 SiO_x 粉末に、人造黒鉛 (平均粒子径 $3\mu\text{m}$) を炭素の割合が50% [$\text{SiO}_x : \text{C} = 5 : 5$ (重量比)] となるように加え SiO_x 粉末と黒鉛との混合物を得た。この SiO_x 粉末と黒鉛との混合物を用いて、実施例1と同様の方法にて負極及び評価用リチウムイオン二次電池を作製し、充放電試験を行った。結果を表1に示す。

【0044】

【表1】

	SiO_x /黒鉛の 平均粒子径比 $d_{50}(\text{A})/d_{50}(\text{B})$	最大放電容量 [mAh/g]	10サイクル目 [mAh/g]	サイクル保持率 [%]
実施例1	2.67	887	867	98
実施例2	4.00	893	857	96
実施例3	2.67	719	698	98
実施例4	1.60	863	723	84
比較例1	2.67	763	511	67
比較例2	4.00	783	556	71

【0045】

【発明の効果】本発明によれば、高容量かつ優れたサイ※

※クル性を示す非水電解質二次電池を与える非水電解質二次電池用負極材が得られる。

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